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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C08F 10/00, 4/642, 4/60

A1

(11) International Publication Number: WO 91/0350

(43) International Publication Date: 21 March 1991 (21.03.91

(21) International Application Number: PCT/BE89/00043

(22) International Filing Date: 8 September 1989 (08.09.89)

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(81) Designated States: AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CM (OAPI patent), DE*, DE (European patent)*, DK, FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL, NL (European patent), NO, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent).

Published
With international search report.

(54) Title: CATALYST AND PROCESS FOR THE POLYMERIZATION OF OLEFINS

(57) Abstract

The use of a concentrated alumoxane solution as cocatalyst for the polymerization of olefins with a homogeneous metallocene-type catalyst of formula $(Cp)_mR_nMQ_k$, wherein Cp is a substituted or unsubstituted metallocene, R is an optional structural bridge between two Cp rings, M is a transition metal from groups 4 and 5, Q is H or alkyl or alkenyl or halogen, $m = 1\text{-}3$, $n = 0$ or 1 and $m + k$ equals the oxidation state of M, provides better yields at lower Al/M ratio. Also provided are a homogeneous catalyst system, a process for preparing same, and a process for the polymerization of olefins, preferably to produce syndiotactic polypropylene.

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CATALYST AND PROCESS FOR THE POLYMERIZATION OF OLEFINS

The present invention relates to a catalyst and a process for the polymerization and copolymerization of olefins, particularly useful for the polymerization of ethylene and propylene and for the copolymerization of ethylene or propylene with other olefins having 3 or more carbon atoms including alpha-olefins such as, for example, propylene, isobutene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, or cyclic olefins such as norbornene.

The invention is particularly concerned with the polymerization of propylene to form isotactic or syndiotactic polypropylene.

The invention further relates to a homogeneous catalyst system comprising a transition metal-containing catalyst component and an alumoxane as cocatalyst.

Traditionally, olefins have been polymerized or copolymerized in the presence of hydrocarbon-insoluble catalyst systems comprising a transition metal compound and an aluminium alkyl. More recently, active homogeneous catalyst systems comprising a bis(cyclopentadienyl) titanium dialkyl or a bis(cyclopentadienyl) zirconium dialkyl, an aluminium trialkyl and water have been found to be useful for the polymerization of ethylene.

European Patent n° 35,242 discloses a process for preparing ethylene polymers and atactic propylene polymers in the presence of a halogen-free Ziegler catalyst system comprising (1) a cyclopentadienyl compound of the formula $(cyclopentadienyl)_nMeY_{4-n}$ in which n is an integer from 1 to 4, Me is a transition metal, especially zirconium, and Y is either hydrogen, a C_1-C_5 alkyl or metallo alkyl group or a radical having the general formula CH_2AlR_2, $CH_2CH_2AlR_2$ or $CH_2CH(AlR_2)_2$ in which R represents a C_1-C_5 alkyl or metallo alkyl group, and (2) an alumoxane. Additional teachings of homogeneous catalyst systems comprising a metallocene and alumoxane are European Patent n° 69,951 and U.S. Patent 4,404,344.

An advantage of the metallocene-alumoxane homogeneous catalyst system is the good activity obtained for olefin polymerization. Nevertheless, the catalyst systems suffer from a disadvantage, that is, the ratio of alumoxane to metallocene is high, for example, in the order of 3,000 to 1 or greater. Such voluminous amounts of alumoxane

would require extensive treatment of polymer product obtained in order to remove the undesirable aluminium.

It has already been proposed in International Application WO87/02991 to reduce the alumoxane to transition metal ratio by using a heterogeneous supported catalyst system comprising both a metallocene and a non-metallocene compound, the latter not requiring alumoxane.

It would thus be highly desirable to provide a metallocene-based catalyst which is commercially useful for the polymerization of olefins wherein the aluminium to transition metal ratio is reduced compared with the known homogeneous systems.

In accordance with the present invention, there is provided a homogeneous catalyst system for olefin polymerization and copolymerization, said system comprising (i) a metallocene transition metal catalyst and (ii) an alumoxane cocatalyst, said alumoxane being provided under the form of a solution of at least 20 wt%.

In accordance with a preferred embodiment of the invention, said catalyst system for olefin polymerization and copolymerization is provided with a molar ratio alumoxane/transition metal compound lower than 2000.

In another embodiment of this invention there is provided a process for the (co)polymerization of olefins in the presence of the new catalyst system. The process, by means of the catalyst, provides the capability of producing polymers with a higher yield with respect to the alumoxane. The process also provides the capability of producing polymers using a lower alumoxane/transition metal compound molar ratio.

The alumoxanes employed as cocatalyst in the system are themselves the reaction products of an aluminium trialkyl with water.

The alumoxanes are well known in the art and comprise oligomeric, linear and/or cyclic alkyl alumoxanes represented by the formulae :

$R\text{-}(AlR\text{-}O)_n\text{-}AlR_2$ for oligomeric, linear alumoxanes, and

$(\text{-}AlR\text{-}O)_m$ for oligomeric, cyclic alumoxanes,

wherein n is 1-40, preferably 1-20, m is 3-40, preferably 3-20 and R is a C_1-C_8 alkyl group and preferably methyl. Generally, in the preparation of alumoxanes from, for example, trimethylaluminium and water, a mixture of linear and cyclic compounds is obtained.

The alumoxanes can be prepared in a variety of ways. Preferably, they are prepared by contacting water with a solution of aluminium trialkyl, such as, for example, trimethylaluminium, in a suitable organic solvent such as benzene, toluene or xylene. For example, the aluminium alkyl is treated with water in the form of a moist solvent. In a preferred method, there is used alumoxane under the form of a solution of at least 20 wt%, most preferably a near-saturated solution.

The present invention employs at least one metallocene compound in the composition of the catalyst system. A metallocene or cyclopentadienide is an organometallic coordination compound which is a cyclopentadienyl derivative of a transition metal. The metallocenes usefully employed in accordance with this invention contain one, two or three cyclopentadiene rings or derivatives thereof, preferably two. The transition metal is selected from Group 4 or 5 (formerly known as IVB or VB) metals, preferably titanium, zirconium, hafnium and vanadium, and especially titanium and zirconium. The cyclopentadienyl ring can be unsubstituted or contain substituents such as, for example, hydrocarbyl substituents.

These metallocenes can be represented by the general formulae :

$$(Cp)_m R_n M Q_k$$

wherein each Cp is the same or different and is a cyclopentadienyl or a cyclopentadienyl substituted by one or more hydrocarbyl radical such as alkyl, alkenyl, aryl, arylalkyl or alkylaryl radical having from 1 to 20 carbon atoms, R is a structural bridge between two Cp rings, M is a transition metal selected from groups 4 or 5, each Q is the same or different and is any substituent not interfering with the active $(Cp)_m R_n M$ part of the metallocene, m=1-3, n=0 or 1, and k is such that the sum of m+k is equal to the oxidation state of M.

Typical structural bridges R between Cp rings include for example alkylene radicals having from 1 to 4 carbon atoms, and heteroatomic bridges such as dialkyl germanium or silicium, alkyl phosphine or alkyl amine. Typical possibilities of Q include hydrides or hydrocarbyl groups having from 1 to 20 carbon atoms or halogens or alkenyl groups having from 2 to 20 carbon atoms.

Preferred metallocene catalysts are those disclosed in European Patent Application 89870079.4, wherein m=2 and n=1, and wherein the

cyclopentadienyl rings are sterically differently substituted, their use leading to the formation of substantially syndiotactic polymers.

The conditions under which the polymerization or copolymerization of olefins may be conducted are known in the art. The polymerization may be conducted by a solution, slurry, or bulk technique, generally at a temperature in the range of about 0°-160°C or even higher, and under atmospheric, subatmospheric, or superatmospheric pressure conditions, and conventional polymerization adjuvants, such as hydrogen may be employed if desired. It is generally preferred to use the catalyst composition at a concentration such as to provide about 0.000001-0.005%, most preferably about 0.00001-0.0003%, by weight of transition metal based on the weight of monomer(s), in the polymerization of ethylene or propylene, alone or with one or more higher olefins.

Examples of polymerization procedure that may be used are disclosed in European Patent Application n° 284.708, incorporated herein by reference.

Before the actual polymerization step, a prepolymerization step may be provided. Prepolymerization conditions are known in the art, as described for example in European Patent Application n° 279.153.

The polymers produced by the catalyst and process of this present invention are capable of being fabricated into a wide variety of articles, as is known for homopolymers of ethylene or propylene and copolymers thereof.

The invention will be further described by way of the following examples.

Example 1

a. Synthesis of the catalyst

Isopropyl (or dimethyl ANSA(1)) fluorenyl cyclopentadienyl zirconium dichloride was prepared according to Method B disclosed in European Patent Application 89870079.4.

b. Preparation of the catalyst system

In a glove box under argon atmosphere, the catalyst system was prepared by dissolving 2 mg of the hereabove catalyst in 0.45 ml of a 36.6 wt% solution of methylalumoxane in toluene, resulting in a bright pink solution. Thus, the composition of said system was as follows :

- catalyst	2 mg	Al/Zr = 500 mole/mole
- cocatalyst	132.0 mg	
- toluene	229 mg	

The catalyst system was prepared 20 minutes before its being used (precontacting time).

c. Polymerization procedure

A 4.5 l stainless steel reactor equipped with an inclined blade stirrer and with appropriate inlets for monomer and catalyst system feeding was purged with nitrogen and cooled to about 15°C by flushing with 0.5 l of liquid propylene.

The reactor was loaded with 1.5 l of liquid propylene at 15°C, and the stirrer was rotated at 250 rpm.

The catalyst system was injected and flushed into the reactor with another 1.5 l of liquid propylene at 15°C.

The temperature of the reactor was then increased to 60°C and the polymerization reaction was continued for one hour. The reaction was stopped by cooling to 0°C and venting off any unreacted monomer.

A polypropylene fluff having nicely spherical particles was collected as a wet powder and dried overnight at 50°C under vacuum, yielding 306.7 g of powder.

d. Product characteristics

- melt flow index	5.20 g/10 min	ASTM D1238	(2.16 kg/190°C)
- bulk density	0.21 g/cm^3	ASTM D1898	

Example 2

The procedure of example 1 was repeated identically with the exception that 0.5 ml of a 30 wt% solution of methylalumoxane was used. Thus, the composition of the catalyst system was as follows :

- catalyst 2 mg Al/Zr = 500 mole/mole
- cocatalyst 132.0 mg
- toluene 308 mg

The yield was of 307.4 g of dry polypropylene fluff (not significantly different from that of example 1) having a melt flow index of 4.43 g/10 min and a bulk density of 0.23 g/cm^3.

Comparative example A

The procedure of example 1 was repeated identically with the exception that 1.5 ml of a 10 wt% solution of methylalumoxane was used. Thus, the composition of the catalyst system was as follows :

- catalyst 2 mg Al/Zr = 500 mole/mole
- cocatalyst 132.0 mg
- toluene 1188 mg

The yield was of 151.0 g of dry polypropylene fluff having a melt flow index of 4.40 g/10 min and a bulk density of 0.19 g/cm^3.

Examples 3 to 6 (36% MAO) and comparative examples B to E (10% MAO)

The procedure of example 1 was repeated identically with the exceptions as stated in the Table, which also states the products characteristics. The Table also contains data relating to examples 1, 2 and A for convenience.

Table

Ex. n°	Cat. mg	Cocat. mg	Toluene mg	Al/Zr mol/mol	Yield g	MFI g/10 min	d g/cm^3
1	2	132	229	500	153.3	5.20	0.21
2	2	132	308	500	153.7	4.43	0.23
A	2	132	1188	500	75.5	4.40	0.19
3	2	264	458	1000	193.0	4.00	0.35
B	2	264	2376	1000	127.1	3.73	0.18
4	3	367	636	930	185.2	3.68	0.23
C	3	396	3564	1000	144.1	3.91	0.19
5	2	367	636	1400	240.0	4.37	0.24
D	2	396	3564	1500	196.2	3.55	0.25
6	2	792	1374	3000	274.6	3.28	0.21
E	2	792	7128	3000	211.1	3.42	0.32

It can be seen that lower Al/Zr ratios may be used favourably when concentrated methylalumoxane solutions are employed.

Claims

1. Use of a concentrated alumoxane solution as cocatalyst for the polymerization or copolymerization of olefins with a homogeneous metallocene-type catalyst of general formula $(Cp)_mR_nMQ_k$ wherein each Cp is the same or different and is a cyclopentadienyl or a cyclopentadienyl substituted by one or more hydrocarbyl radical such as alkyl, alkenyl, aryl, arylalkyl or alkylaryl radical having from 1 to 20 carbon atoms, R is a structural bridge between two Cp rings, M is a transition metal selected from groups 4 or 5, each Q is the same or different and is a hydride or a hydrocarbyl group having from 1 to 20 carbon atoms or an alkenyl group having from 2 to 20 carbon atoms or a halogen, m=1-3, n=0 or 1, and k is such that the sum of m+k is equal to the oxidation state of M.
2. Use of an alumoxane solution according to claim 1, characterized in that said solution contains at least 20 wt% of alumoxane.
3. Use of an alumoxane solution according to either of claims 1 or 2, characterized in that the molar ratio alumoxane/catalyst is lower than 2000.
4. Use of an alumoxane solution according to claim 3, characterized in that the molar ratio alumoxane/catalyst is lower than 1000.
5. Use of an alumoxane solution according to any one of the preceeding claims, characterized in that the alumoxane is methylalumoxane.
6. Homogeneous catalyst system for olefin polymerization and copolymerization, said system comprising (i) a metallocene-type catalyst of general formula $(Cp)_mR_nMQ_k$ wherein each Cp is the same or different and is a cyclopentadienyl or a cyclopentadienyl substituted by one or more hydrocarbyl radical such as alkyl, alkenyl, aryl, arylalkyl or alkylaryl radical having from 1 to 20 carbon atoms, R is a structural bridge between two Cp rings, M is a transition metal selected from groups 4 or 5, each Q is the same or different and is a hydride or a hydrocarbyl group having from 1 to 20 carbon atoms or an alkenyl group having from 2 to 20 carbon atoms or a halogen, m=1-3, n=0 or 1, and k is such that the sum of m+k is equal to the oxidation state of M, and (ii) an alumoxane cocatalyst, said alumoxane being provided under the form of a

solution of at least 20 wt%.

7. Homogeneous catalyst system according to claim 6, characterized in that the molar ratio alumoxane/catalyst is lower than 2000.
8. Homogeneous catalyst system according to claim 7, characterized in that the molar ratio alumoxane/catalyst is lower than 1000.
9. Homogeneous catalyst system according to any one of claims 6, 7 or 8, characterized in that the alumoxane is methylalumoxane.
10. Process for producing a homogeneous catalyst system for olefin polymerization and copolymerization, said system comprising (i) a metallocene-type catalyst of general formula $(Cp)_mR_nMQ_k$ wherein each Cp is the same or different and is a cyclopentadienyl or a cyclopentadienyl substituted by one or more hydrocarbyl radical such as alkyl, alkenyl, aryl, arylalkyl or alkylaryl radical having from 1 to 20 carbon atoms, R is a structural bridge between two Cp rings, M is a transition metal selected from groups 4 or 5, each Q is the same or different and is a hydride or a hydrocarbyl group having from 1 to 20 carbon atoms or an alkenyl group having from 2 to 20 carbon atoms or a halogen, m=1-3, n=0 or 1, and k is such that the sum of m+k is equal to the oxidation state of M, and (ii) an alumoxane cocatalyst, characterized in that said alumoxane is provided under the form of a solution of at least 20 wt%.
11. Process according to claim 10, wherein the molar ratio alumoxane/catalyst is lower than 2000.
12. Process according to claim 11, wherein the molar ratio alumoxane/catalyst is lower than 1000.
13. Process according to any one of claims 10, 11 or 12, wherein the alumoxane is methylalumoxane.
14. Process for the polymerization or copolymerization of olefins in the presence of a catalyst system comprising (i) a metallocene-type catalyst of general formula $(Cp)_mR_nMQ_k$ wherein each Cp is the same or different and is a cyclopentadienyl or a cyclopentadienyl substituted by one or more hydrocarbyl radical such as alkyl, alkenyl, aryl, arylalkyl or alkylaryl radical having from 1 to 20 carbon atoms, R is a structural bridge between two Cp rings, M is a transition metal selected from groups 4 or 5, each Q is the same or different and is a hydride or a hydrocarbyl group having from 1 to 20 carbon atoms or an alkenyl group having from 2 to 20 carbon atoms or a halogen, m=1-3, n=0 or 1, and k is

such that the sum of $m+k$ is equal to the oxidation state of M, and (ii) an alumoxane cocatalyst, characterized in that said alumoxane is provided under the form of a solution of at least 20 wt%.

15. Process according to claim 14, wherein the molar ratio alumoxane/catalyst is lower than 2000.
16. Process according to claim 15, wherein the molar ratio alumoxane/catalyst is lower than 1000.
17. Process according to any one of claims 14, 15 or 16, wherein the alumoxane is methylalumoxane.
18. Process according to any one of claims 14 to 17, when applied to the polymerization of propylene.

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